

# SCIENCE FOR GLASS PRODUCTION

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## SINTERING OF CHEMICAL BATCHES

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Sintering of x-ray-amorphous and crystallized chemical batches is investigated using the continuous shrinkage method and the standard method for powder sinterability evaluation. The water absorption, open porosity, and apparent density of the obtained samples are determined.

The low-temperature chemical synthesis method is promising for the development of glass ceramics with prescribed properties. The method involves synthesis of the batch and sintering of finely disperse powders whose particles initiate the crystallization processes [1]. The absence of oxides acting as crystallization catalysts and technological additives in the initial mixture facilitates the production of glass ceramic materials with a set of physicochemical properties close to the projected ones.

The present study considers the sintering process in chemical batches of the  $\text{LiO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$  system with the stoichiometric and actual composition. The composition used in practice contained the vitreous phase designed in accordance with the fractional combination method. The batch was synthesized by decantation of saturated solutions of metal (Li, Al, Ba) nitrates and the product of tetraethoxysilane hydrolysis in ethyl alcohol. The resulting solution was subjected to hydrolysis at a temperature of 60–70°C for 5 h, drying at the same temperature for 24 hours, and dehydroxylation and removal of  $\text{NO}_3$  nitric groups at temperatures of 60–600°C [2].

The process of sintering in the x-ray-amorphous chemical batch with the stoichiometric and actual composition was investigated at the Chair of Ceramics at the D. I. Mendelev Russian Chemical Engineering University using the continuous shrinkage method. The temperature dependence of sample shrinkage is shown in Fig. 1.

Intense consolidation of the material is observed within the temperature range of 600–800°C. The consolidation process is accompanied by crystallization of the material. According to the x-ray phase analysis,  $\beta$ -quartz solid solution is crystallized in the stoichiometric composition batch,

and the actual composition batch produces hexagonal barium aluminosilicate along with the  $\beta$ -quartz solid solution [3, 4].

A further increase in the temperature up to 1000°C (the stoichiometric composition) and up to 1100°C (the actual composition) activates and brings to completion the crystallization of the material. The sintering process within the specified temperature range is stopped by intense crystallization which ends with the formation of a finely crystalline structure with uniformly distributed micropores (up to 1000°C), since the high-melting residual vitreous phase does not have time to fill the emerging voids. Within these voids the growth of cristobalite takes place. The existence of this phase [4] which is characterized by high positive values of the coefficient of thermal linear expansion (TCLE) which contrast

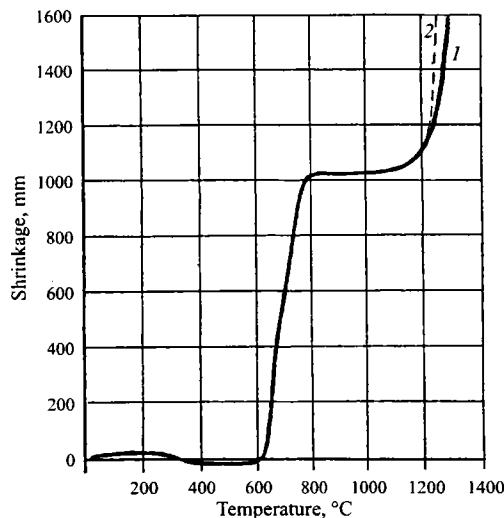


Fig. 1. Temperature dependence of the shrinkage of the x-ray-amorphous batch of stoichiometric (1) and actual (2) mixtures.

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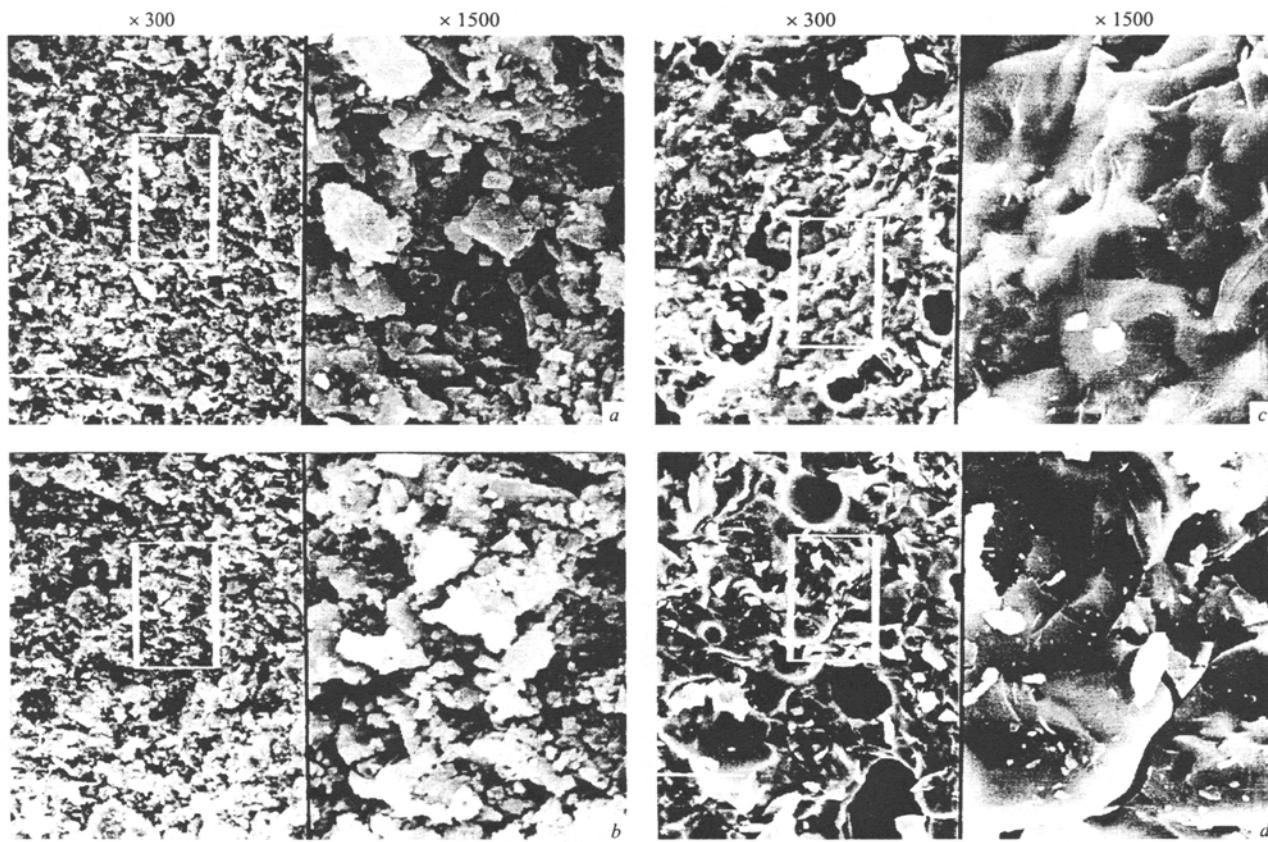


Fig. 2. Electron microscope photos of x-ray amorphous batch of the actual mixture heat-treated at temperatures of 800°C (a), 900 (b), 1150°C (c), and 1250°C (d).

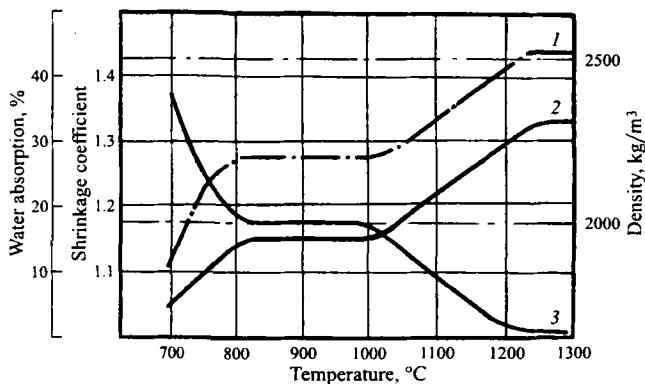


Fig. 3. Density (1), shrinkage coefficient (2), and water absorption of the x-ray-amorphous batch versus firing temperature.

with the TCLEs of both types of solid solutions and the residual vitreous phase, is not manifested in the overall CTLE of the material, which implies the existence of defects in the material.

At a temperature exceeding 1000°C, the residual vitreous phase after the formation of cristobalite is deprived of  $\text{SiO}_2$  and becomes less viscous, and the sintering process is intensified, which is indicated by the appearance of the second

ascending branch on the shrinkage curve. The sintering of the actual composition batch is additionally intensified due to partial dissolution of the hexagonal barium aluminosilicate.

The high degree of dispersion of the batch (particle size of 0.1 – 2.0  $\mu\text{m}$ ) heat-treated at temperatures of 800 – 900°C is supported by electron microscope photographs made with a raster microscope (Fig. 2). The sintering of the crystallized batch particles takes part at temperatures of 1150 – 1250°C.

The semidry-press molding method was used to produce samples of the x-ray-amorphous batch and the batch crystallized at temperatures of 800, 1000, and 1150°C.

The x-ray-amorphous batch was crushed in a ball mill in propanol medium for 30 min to attain a specific surface area of 1500  $\text{m}^2/\text{kg}$ . The batch crystallized at temperatures of 800, 1000, and 1150°C was milled for 4 – 8 h to attain a specific surface area of 300, 500, and 700  $\text{m}^2/\text{kg}$ . The plasticizing agents were polyvinyl alcohol solution and paraffin. The x-ray-amorphous batch was compressed at a pressure of 50 MPa (and afterward dried at a temperature of 100°C), and the crystallized batch was compressed at 50 – 200 MPa.

In order to study the sintering process, the chemical batch samples were fired at temperatures of 700 – 1300°C, and thereupon their water absorption, shrinkage coefficient,

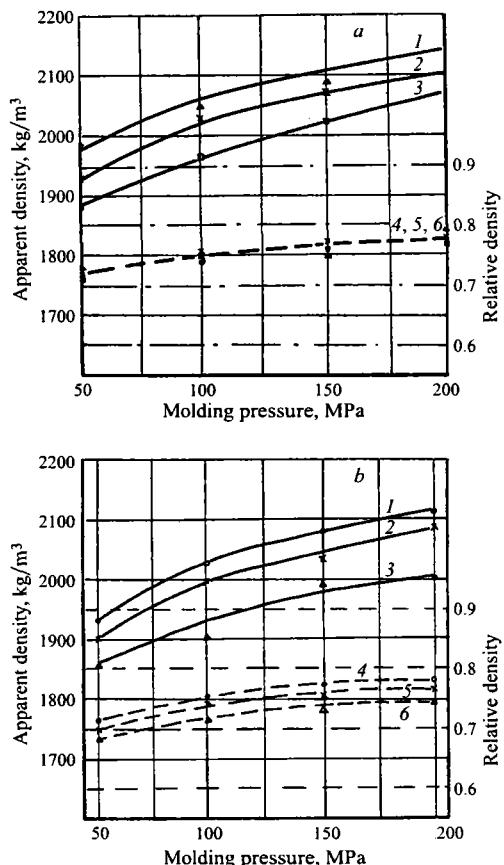


Fig. 4. Dependence of apparent (1–3) and relative (4–6) densities of the batch samples crystallized at a temperature of 1000°C with different paraffin content (a) and different specific surface area (b) on molding pressure. Paraffin mass content: 1, 4) 4%; 2, 5) 6%; 3, 6) 8%; specific surface area: 1, 4) 300 m<sup>2</sup>/kg, 2, 5) 500 m<sup>2</sup>/kg, 3, 6) 700 m<sup>2</sup>/kg.

and density were measured. Data obtained for samples of the x-ray-amorphous batch are presented in Fig. 3.

The shrinkage coefficients of the samples of the x-ray-amorphous batch heat treated at 700–1300°C match the shrinkage coefficients determined from the shrinkage curve obtained under conditions of continuous heating.

As the molding pressure increases (50–200 MPa), the apparent and relative densities of paraffin-containing samples of the batch crystallized at 1000°C also increases (Fig. 4, a). The higher the paraffin content, the stronger the intermediate product. The relative density does not depend on the quantity of the introduced plasticizer. The effect of the dispersion degree of the material on the strength of the samples under various levels of molding pressure was studied on the crystallized batch containing 7% paraffin. The batch dispersion within the limits of 300–700 m<sup>2</sup>/kg contributes to an increase in the apparent and relative densities (Fig. 4b). The water absorption of the batch samples crystallized at temper-

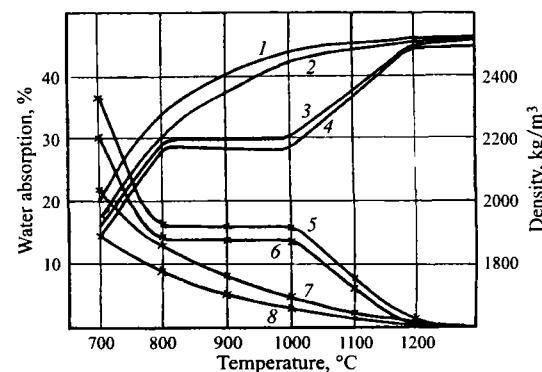


Fig. 5. Density (1–4) and water absorption (5–8) of chemical batch samples depending on firing temperature: 4, 5) 600°C; 3, 6) 800°C; 2, 7) 1000°C; 1, 8) 1150°C.

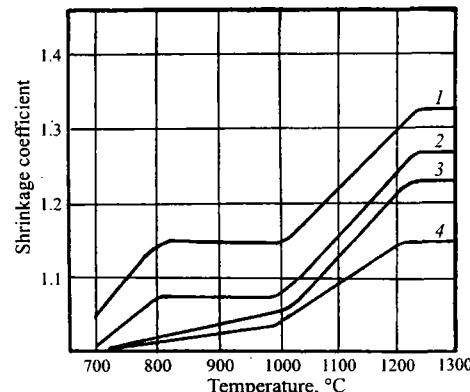


Fig. 6. Shrinkage coefficient of chemical batch samples depending on firing temperature: 1) 600°C; 2) 800°C; 3) 1000°C; 4) 1150°C.

atures of 800, 1000, and 1150°C are given in Fig. 5, and the shrinkage coefficient is shown in Fig. 6.

The results of the study of the sintering process can be used to substantiate the optimum firing conditions for the materials produced on the basis of x-ray-amorphous and crystallized batches.

## REFERENCES

1. R. Ya. Khodakovskaya, "Current state and prospects of research in the field of glass ceramics," in: *Catalyzed Crystallization of Glass* [in Russian], Moscow (1986).
2. I. D. Tykachinskii, V. V. Gorbachev, E. P. Dain, and V. A. Leshina, "Structural transformations in chemical batches of the Li<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system," *Izv. AN SSSR Ser. Neorg. Mater.*, **25**(3), 415–418 (1989).
3. E. P. Dain and V. A. Leshina, "A study of crystallization processes in chemical batches of the Li<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system," in: *Catalyzed Crystallization of Glass* [in Russian], Moscow (1986).
4. V. A. Leshina and L. I. Shvorcova, "Crystallization of amorphous chemical batches of the Li<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system," *Steklo Keram.*, No. 10, 8–10 (1996).